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(54) Title: ELECTROFLOCCULATOR FOR SOLIDS REMOVAL IN HYDROCARBON PROCESSES

(57) Abstract

The instant invention is directed to a method for removing catalyst particles, having at least about 0.1 wt. % metal in the zero valence state, from hydrocarbon process fluids using an electric field. The invention is further directed to an improved reactor apparatus wherein a hydrocarbon process vessel is attached to an electroflocculating apparatus.

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ELECTROFLOCCULATOR FOR SOLIDS REMOVAL IN HYDROCARBON PROCESSES

Field of the Invention

The present invention is directed to a continuous method of removing solid catalyst particles from hydrocarbon process fluids, including Fischer-Tropsch process fluids, using an electric field preferably an electric field generated by an electroflocculating apparatus. The invention is further directed to such apparatus.

Background of the Invention

In most chemical processes involving solid catalyst particles dispersed in a liquid, an easy separation method for removing the catalyst particles from the liquid is considered critical. Despite the fact that smaller catalyst particles can promote higher reactor productivity and product selectivity, larger particles are used to avoid the problems encountered in separating small catalyst particles or in confining particles in the process vessel using conventional filtration or settling techniques.

Summary of the Invention

Thus, one aspect of the instant invention advantageously allows catalyst free product fluid to be removed from a process without the use of filters which become blinded (clogged) necessitating interrupting the process for filter replacement or cleaning. Applicants have discovered a way of separating particles from process fluids. The method of the instant invention has no effect on the catalyst surface area, particle density, particle size, or catalyst activity.

The instant invention is directed to a method for separating solid catalyst particles from hydrocarbon process fluids comprising the steps of:

(a) introducing a mixture of a process fluid and solid catalyst particles, said solid catalyst particles containing at least about 0.1 wt.% metal in the zero valence state, and wherein said process fluid exhibits an electric conductivity less than about 1×10^{-10} ohm^{-1} m^{-1} into an electric field, wherein said electric field has an electric field strength of greater than 100 volts/cm and a frequency of about 0.1 hertz to about 5000 hertz, to produce agglomerated solid catalyst particles;

(b) separating, through gravity, said agglomerated solid catalyst particles from said hydrocarbon process fluid.

In a preferred embodiment of the invention, the process further comprises step:

(c) removing said separated agglomerated solid catalyst particles from said electric field to produce deagglomerated solid catalyst particles.

In an even more preferred embodiment, the process further comprises step:

(d) reintroducing said deagglomerated solid catalyst particles into the hydrocarbon process reaction zone. Thus, in a preferred embodiment a recirculating process can be conducted.

The invention is further directed to an improved apparatus for the continuous removal of solid catalyst particles containing at least 0.1 wt.% metal in the zero valence state, from process fluids following reaction wherein the improvement comprises attaching a hydrocarbon process vessel to an

electroflocculating apparatus, said electroflocculating apparatus comprising:

(a) a hollow shell having at least one inlet for acceptance of a mixture of process fluids and solid catalyst particles, said catalyst particles containing at least 0.1 wt.% metal in the zero valence state, a top outlet for drawing off process fluids having solid catalyst particles removed therefrom, and a bottom outlet for expelling deagglomerated catalyst particles;

(b) a plurality of electrodes in functional relation with said hollow shell, wherein said electrodes extend above said hollow shell inlet and;

(c) a high voltage power source coupled to said electrodes and capable of producing an electric field strength of greater than 100 volts/cm and a frequency of about 0.1 to about 5000 hertz within said hollow shell:

Hence, it can be seen that the apparatus allows for the continuous removal of solid catalyst particles from process fluids and conveyance of the removed solid catalyst particles, which deagglomerate once removed from the electric field back into the reaction zone, if desired. The electroflocculator can be located within or without (outside) the reactor.

Brief Description of the Drawings

Figure 1 depicts one possible electroflocculating apparatus where the electroflocculator is located inside a hydrocarbon synthesis bubble column.

Figure 2 shows another possible electroflocculator set up.

Detailed Description of the Invention

The instant invention teaches a method for separating catalyst particles from process fluids having such particles suspended therein. The method is capable of separating particles which are 1 micron in size up to and including a 0.3 cm particles. The invention can remove suspended particles from any type of hydrocarbon liquid. The invention is particularly useful for removing catalyst particles from slurry process fluids, particularly bubble column slurry process fluids, ebulating bed processes and stirred process fluids. Advantageously, catalyst particles can be separated from the process fluids in accordance with the instant invention without any pretreatment of the process fluids. Thus, they can be introduced directly into the electroflocculator aparatus from the hydrocarbon reaction vessel.

The invention merely requires that the solid catalyst particles contain at least 0.1 wt.%, based on the total particle weight, of a metal in its zero valence state.

Applicants have discovered that applying an electric field to a process fluid which contains about 0.1 to 50 wt.%, preferably 0.3 to 50 wt.% suspended solid catalyst particles containing at least 0.1 wt.% metal in the zero valence state, causes the solid catalyst particles to be temporarily agglomerated, causing them to settle, through gravity, out of the process fluid enabling the ready removal of process fluid from the fluid/solid mixture. Once the catalyst particles have settled and passed out of the electric field, they deagglomerate to their original size and are usable once again. Hence, they can be immediately returned to the reaction zone without interruption of the process being performed and a recirculating process (which reutilizes the deagglomerated catalyst particles) can be conducted. Thus, the present invention can be utilized to reclaim, e.g., supported Fischer-Tropsch catalysts from slurry

Fischer-Tropsch media. The invention can additionally be used on promoted cobalt catalyst such as rhenium promoted cobalt. For example, the invention can be used to separate a cobalt-rhenium on titania catalyst from Fischer-Tropsch media. The above catalysts are merely illustrative and are not meant to be limiting. The instant invention is capable of removing >95% of the solid catalyst particles directly from the process fluid without the aid of any pretreatment steps.

For illustration, a slurry process fluid can be passed through an electroflocculator, in accordance with the instant invention, whereupon the catalyst particles present will agglomerate and settle to the electroflocculator vessel bottom. Once the catalyst particles are outside of the forces of the electrical field, they deagglomerate. The catalyst particles can then be passed back into the slurry process reaction zone if desired. Process fluid having catalyst particles removed therefrom can be withdrawn from the electroflocculator vessel by any suitable means. In the instant process there is substantially no migration of the catalyst to the electrodes, preferably no such migration will occur.

In an ebulating bed process where liquid is used to fluidize the catalyst, small catalyst fragments entrained from the catalyst bed into the process fluid can likewise be removed and clarified liquid return to the ebulating bed vessel. In this manner, fragments of catalyst particles will not be present in fluid above the ebulating bed and will thus prevent pump clogging when the liquid is recirculated.

The preferred mode of carrying out the instant invention is to pass the process fluid having suspended solid catalyst particle therein through an electroflocculator by utilizing techniques such as the "downcomer" effect commonly practiced in chemical engineering. The flocculator is a vessel equipped with an AC voltage source across two electrodes (hot and ground) capable of producing AC voltage of from about 0.1 hertz, up to and

including about 5000 hertz of current. The electrical field strength produced will be from about 100 volts/cm up to and including about 100,000 volts/cm, preferably from about 200 to about 50,000 volts/cm.

If the process is being conducted in a hydrocarbon synthesis bubble column, the electroflocculator will be equipped with a metal screen, at the area where the process fluid and catalyst particles enter to exclude gas bubbles. The openings of the screen should be adequate to exclude most gas bubbles in the process fluid but allow the passing of the particles. More preferably, the electroflocculator will be equipped with both a baffle and a metal screen. The baffle helps to further exclude gas bubbles. Once the solid catalyst particles experience the electric field, they agglomerate and settle through the opening at the bottom of the electroflocculator. They can thus be readily removed. The departiculated process stream can be collected by any suitable means such as siphoning from near the top of the electroflocculator, decanting, etc.

The instant method can be carried out with an electroflocculator inside the reaction vessel, enabling the agglomerated catalyst particles, which deagglomerate without any change in size, surface area, particle density or catalyst activity, to be passed back into the reaction zone once removed from the electroflocculator. The electroflocculator could alternatively be external to the reaction vessel itself. In the external setup, the deagglomerated particles may be returned to the reaction zone by any suitable means such as pumping.

Applicants believe that once the process fluid/solid catalyst particle mixture enters the electric field, the small catalyst particles, having zero valence metal therein, will experience electric dipole/dipole interactions and will flocculate to agglomerates that exhibit a much higher settling velocity than deagglomerated particles. Because gas will have preferably been removed from the fluid, there will be a driving force for the

liquid to flow downward due to the Downcomer effect. This Downcomer effect will be countered by any process fluid removal during settling. Provided the net rising velocity of the process liquid is less than the settling velocity of the agglomerated particles, most particles can be removed through enhanced settling of the agglomerates. If desired, the electroflocculator may be equipped with a screen or filter at the product withdrawal outlet to filter any solid residual catalyst particles that might be present near the siphoning outlet due to inadequate residence times.

The horizontal cross-sectional area of the upper zone of the electroflocculator, the zone of high electric field above the entrance and below the exit port for clarified product, will be sized such that the liquid upflow velocity in this zone is about a factor of 2 to about 40 of the Stokes velocity of the particles being separated. The higher the electric field used, as well as the zero valence metal content of the particles, the higher the factor that can be used. The height of this zone should be such that it allows a residence time of at least 0.1 minutes, preferably at least about 0.5 minutes. The longer the residence time, the greater the departiculation efficiency.

The apparatus which will preferably be used to carry out the method of the instant invention will consist of a reactor vessel equipped with an electroflocculator attached to the outside of the reactor or present within the reactor. Additionally, the electrodes of the electroflocculator may be within or external to the flocculator shell. The electrodes need only produce an electric field which penetrates the process fluid having suspended catalyst particles therein, they needn't directly contact the fluid. The electroflocculator on the outside of the reactor vessel will be piped to the reactor and will contain a valve for process fluid drawoff. The bottom of the flocculator will be piped back into the reactor to enable the agglomerated catalyst particles to be removed from the electric field, deagglomerated and passed back into the reactor to participate in the reaction

being carried out if a recirculating process is desired.

When the electroflocculator is contained within the reactor, its vessel walls will preferably have a portion composed of wire mesh of about 200-2000 micron opening size, which will allow the slurry process fluid to flow into the electro-flocculator. The bottom of the flocculator will be open, allowing agglomerated particles to pass out of the flocculator and into the process vessel. A portion of the flocculator, preferably the top, will protrude from the reactor vessel, enabling process fluid having catalyst removed therefrom to be siphoned off. However, if, e.g. an ebulating bed system is being used, the process fluid withdrawal port will be inside the process vessel allowing liquid to be returned to the reaction zone.

In a nonlimiting embodiment of the electroflocculator apparatus, the electroflocculator is located inside a hydrocarbon synthesis bubble column reactor. It consists of a hollow metal shell (A) which serves as a ground electrode, a center electrode (B) connected to a high voltage source (C) which electrode is insulated from the shell (A). Slurry process fluid enters through ports (D) which are metal screens and serve also as grounded grid electrodes. The bottom of the shell is open (E) to the reactor to allow for deagglomerated particles to be expelled from the shell. The top of the shell is connected to a tube (F) which serves as a drawoff port for the removal of product fluid. The efficiency of the cylinder has been increased by the addition of a baffle plate (G) external to the shell beneath the screen. The baffle prevents gas bubbles from contacting the screen. Removal of gas bubbles sets up a gradient which promotes the continuous flow of slurry from the reactor into the shell and exit through the opening (E) due to the Downcomer effect.

In another nonlimiting embodiment of the apparatus, the system comprises a shell (A) equipped with an electrode pair consisting of a metal rod (B) connected to a high voltage source (D) and a metal mesh screen (C) connected to the ground. A

recirculating pump (H) is used to pump feed to the electro-flocculator through port (E). Concentrated slurry exits the flocculator via exit port (F) and is then recirculated via the pump. Departiculated raffinate is withdrawn via port (G).

The above setups are merely illustrative, not limiting.

The process fluids which are clarified by use of the instant invention have a dielectric constant of about 2 to about 4, preferably about 2 to about 3. They exhibit an electric conductivity less than about 1×10^{-10} ohm^{-1} m^{-1}, preferably less than 5×10^{-11} ohm^{-1} m^{-1}.

The following examples are for illustration and are not meant to be limiting.

The experiments were carried out in a 1 7/8" ID by 5.5" long glass vessel fitted with an electrode pair consisting of a 1.7"D x 3"L cylindrical metal screen and a central electrode. The electrodes were connected to the terminals of a high voltage power source capable of generating up to 10 thousand volts of electric potential at frequencies ranging from 40 hertz to 250 hertz.

Slurries of solid particles of 63 micron cobalt on porous TiO_2 particles with ~0.3 cc/gm pore volume with Co in its zero valence and containing about 11.5 wt.% of the above catalyst or 22 microns of conventional Fischer-Tropsch iron catalyst dispersed in hydrocarbon oil were loaded to the surge vessel and pumped through the electroflocculator described above. It was found that whenever a voltage between 2000 and 4000 volts/cm electric field with frequency between about 40 hertz to about 250 hertz was applied to the electrodes, the effluent stream from the vessel turned in color from dark to clear, indicating a significant reduction of solids content in the stream. In fact, as shown in Table 1, the analysis of the solids content in tests at 4000 volts/cm electric field and about 200 hertz indicated that

the electric field in the electroflocculator reduced the solids in the stream by 93 to 97%.

The experiments show that in this case the electroflocculator was capable of removing fine particles from a slurry of a nonaqueous nonelectrolitic liquid with electrical conductivity of 2×10^{-13} ohm^{-1} m^{-1} and dielectric constant of 2.02.

TABLE 1

RESULTS OF ELECTROFLOCCULATION DEPARTICULATION TESTS WITH CATALYST IN HYDROCARBON LIQUID*

Test	Catalyst Type	Flow Rate cc/Min.	Solids in Raffinate when High Volt. On Gm/cc	Solids in Raffinate when High Volt. Off Gm/cc	% Solids Removal
A	Co/Re on TiO_2** Dp = 63 μ	480	Less than 0.0040	0.0625	Greater than 93.6
B	Co/Re on TiO_2** Dp = 63 μ	250	Less than 0.0048	0.1680	Greater than 97.2
C	Conventional Fischer-Tropsch Iron Catalyst (Fe; Cu; K; Si) Dp = 22 μ	140	Less than 0.0028	0.0531	Greater than 94.8

* Hydrocarbon oil of viscosity ~1.8 cP
** Activated and passified
Dp = Mean particle size

A second series of experiments were carried out in an apparatus shown in Figure 2 which was designed to simulate the operation of which was designed to simulate the operation of an electroflocculator to confine catalyst in a chemical reactor. A 1 7/8" ID by 5.5" high glass vessel was fitted with an electrode pair consisting of a 1.7"D x 3"L cylindrical metal screen and a central electrode. They were connected to the terminals of a high voltage power source capable of generating up to 10 thousand volts, producing an electric field of 2000 to 4000 volts/cm at frequencies from 50 to 250 hertz. Slurry was fed from a pump into the side of the electroflocculator vessel close to the bottom of the electrode pair at a flow rate of about 1300 cc/min. The solid particles were to be electroflocculated in the zone between the two electrodes, settled to the bottom of the vessel, and removed as a concentrated slurry at flow rates from 840 to 1080 cc/min. The raffinate with solids - removed exited from the top of the vessel at flow rates from 280 to 420 cc/min. In the lab test, the returned concentrated slurry and raffinate streams were remixed to reconstitute the feed for a continuous test to reach steady state.

Batches of slurries of catalysts in hydrocarbon oil with mean particle size of 63 microns and 22 microns were tested at 10 KV and 200 hertz. The results are listed in Table 2. At a flow rate of about 1300 cc/min. of the raffinate stream departiculation efficiencies from 95% to 99.5% were achieved.

To demonstrate that electroflocculation can also be carried out using electrodes insulated from the slurry, a small batch electroflocculation test tube was set up to allow a visual confirmation of the flocculation when the electric voltage was applied to the slurry. In this unit, two aluminum foil electrodes were attached to the outside of the glass tube, and connected to the 10 KV/200 hertz voltage source. In separate tests using conventional Fischer-Tropsch Iron Catalyst (Fe; Cu; K; Si) of 22 micron size and 50 micron particles of 5% platinum on the surface

of alumina each suspended in hydrocarbon liquid as test samples, oth solids were observed to flocculate in the liquid when the high voltage was turned on and deflocculate when the voltage was turned off. Apparently, the electric field can penetrate the glass wall of the test tube and flocculate the solids. Thus, electro-flocculation can also proceed with insulated electrodes.

TABLE 2

RESULTS OF ELECTROFLOCCULATION DEPARTICULATION

Test	Catalyst Type	Feed Stream		Raffinate Stream		Concentrated Slurry Stream		Departiculation Efficiency
		Solids Conc. Gm/cc	Flow Rate cc/Min.	Solids Conc. Gm/cc	Flow Rate cc/Min.	Solids Conc. Gm/cc	Flow Rate cc/Min.	%
D	Co/Re on TiO2** Dp = 63 μ	0.40	1260	0.0022	420	0.60	840	99.5
E	Co/Re on TiO2** Dp = 22 μ	0.21	1340	0.0019	280	0.27	1060	99.1
F	Co/Re on TiO2** Dp = 22 μ	0.21	1370	0.0097	420	0.30	950	95.4

* At 10 KV/~200 Hz
** Activated and passified
Dp = mean particle size

CLAIMS:

1. A method for separating solid catalyst particles from hydrocarbon process fluids comprising the steps of:

(a) introducing a mixture of a process fluid and solid catalyst particles, said solid catalyst particles containing at least about 0.1 wt.% metal in the zero valence state, wherein said process fluid exhibits an electric conductivity less than about 1 x 10^{-10} ohm^{-1} m^{-1}, into an electric field, wherein said electric field has an electric field strength of greater than 100 volts/cm and a frequency of at least about 0.1 hertz and to produce agglomerated solid catalyst particles;

(b) separating, through gravity, said agglomerated solid catalyst particles from said hydrocarbon process fluid.

2. A method according to claim 1, further comprising step (c), removing said separated agglomerated solid catalyst particles from said electric field to produce deagglomerated solid catalyst particles.

3. A method according to claim 2, further comprising step (d), reintroducing said deagglomerated solid catalyst particles into a hydrocarbon process reaction zone.

4. A method according to claim 1 wherein said solid catalyst particles are 1μ to 0.3 cm particles.

5. A method according to claim 1 wherein said mixture of a process fluid and solid catlayst particles contains about .1 to about 50 wt.% of solid catalyst particles.

6. A method according to claim 1 wherein said mixture of process fluid and solid catalyst particles is introduced directly into said electric field without any pretreatment.

7. A method according to claim 1 wherein said method removes >95% of said solid catalyst particles from said mixture of process fluid and solid catalyst particles.

8. An improved reactor apparatus for the continuous removal of solid catalyst particles containing at least 0.1 wt.% metal in the zero valence state, from slurry process fluids following reaction wherein the improvement comprises attaching a hydrocarbon process vessel to an electroflocculating apparatus, said electroflocculating apparatus comprising:

(a) a hollow shell having at least one inlet for acceptance of a mixture of hydrocarbon process fluids and solid catalyst particles, said catalyst particles containing at least 0.1 wt.% metal in the zero valence state, a top outlet for drawing off product and a bottom-outlet for expelling deagglomerated catalyst particles;

(b) a plurality of electrodes in functional relation with said hollow shell, wherein said electrodes extend above said hollow shell inlet and;

(c) a high voltage power source coupled to said electrodes and capable of producing an electric field strength of greater than 100 volts/cm and a frequency of about 0.1 to about 5000 hertz within said hollow shell.

9. An apparatus according to claim 8 wherein said electroflocculator is located within or without the reactor.

10. A method according to claim 1 wherein said process fluid is a slurry, ebulating bed or stirred process fluid.

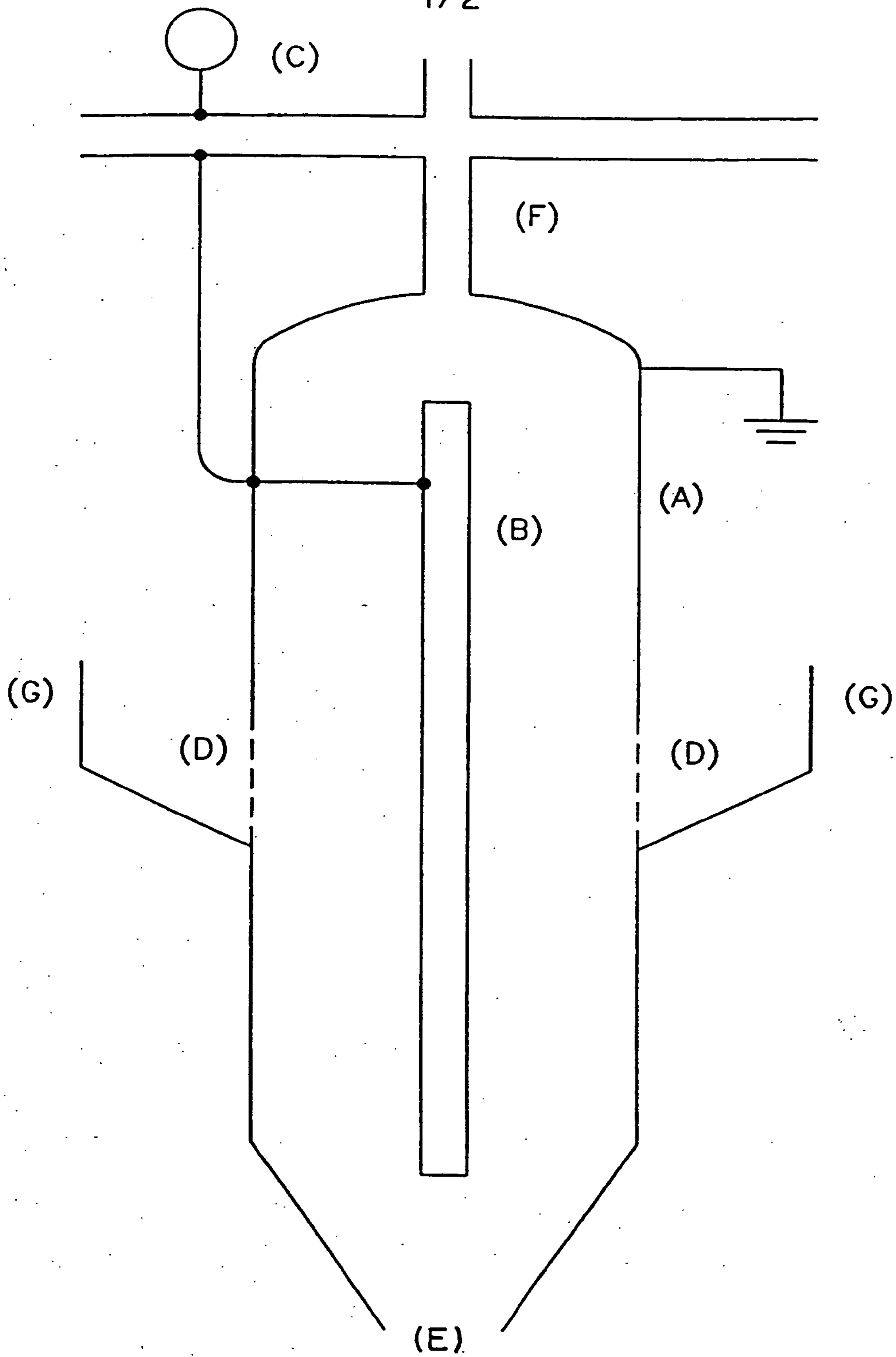

FIG. 1

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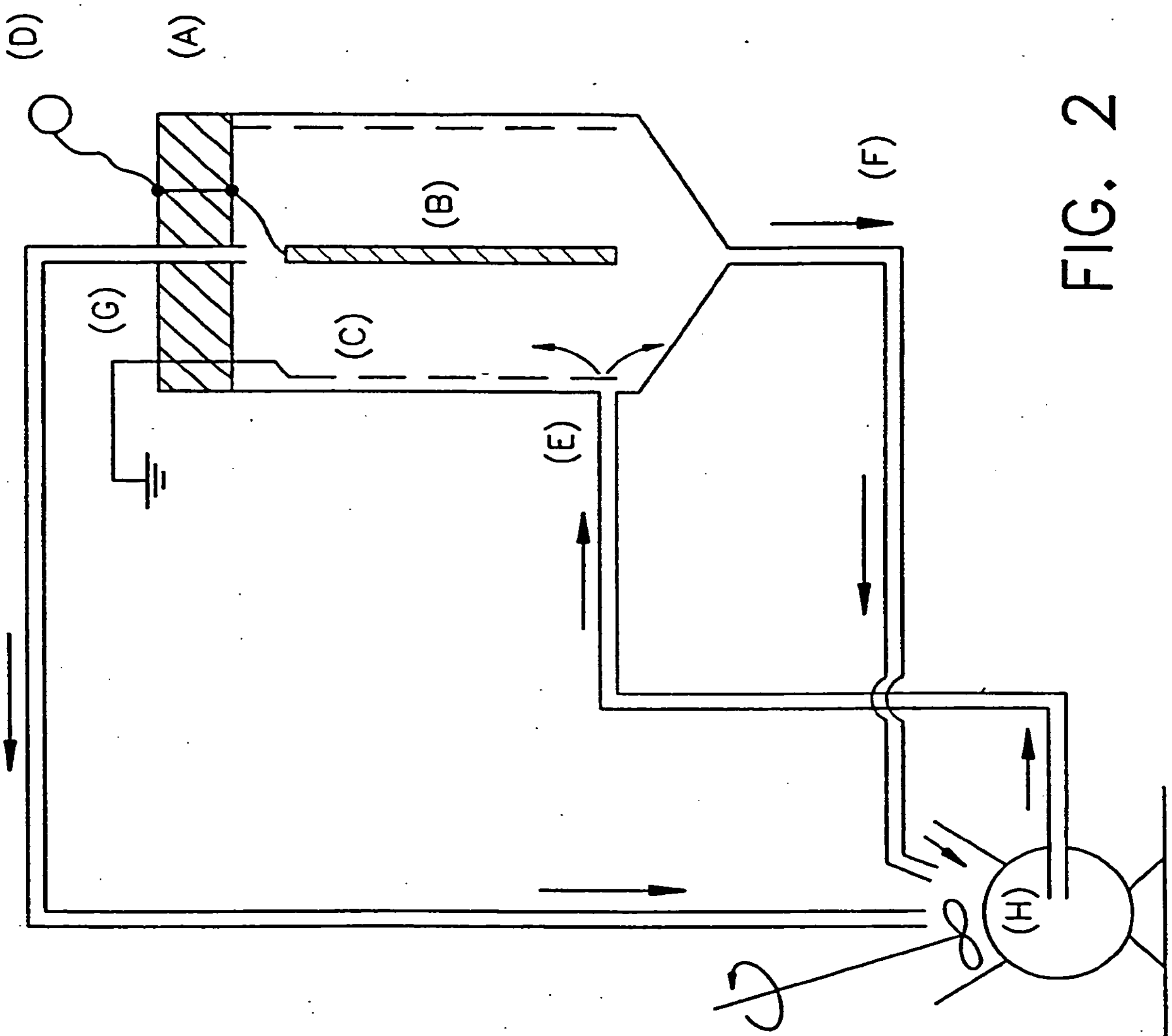

FIG. 2

INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/US 95/05869

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10G32/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,85 03017 (AMERICAN FILTRONA CORPORATION) 18 July 1985 see page 14, line 1; claims 1-22	1-10
A	US,A,3 928 158 (GULF) 23 December 1975 see the whole document	1-10
A	US,A,4 358 379 (INOUE) 9 November 1982	
A	EP,A,0 570 108 (GENERAL ATOMICS) 18 November 1993	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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1

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Michiels, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-8503017	18-07-85	US-A-	4579637	01-04-86
		AU-A-	3836685	30-07-85
		CA-A-	1240953	23-08-88
		EP-A-	0167619	15-01-86
US-A-3928158	23-12-75	NONE		
US-A-4358379	09-11-82	NONE		
EP-A-570108	18-11-93	US-A-	5308586	03-05-94
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